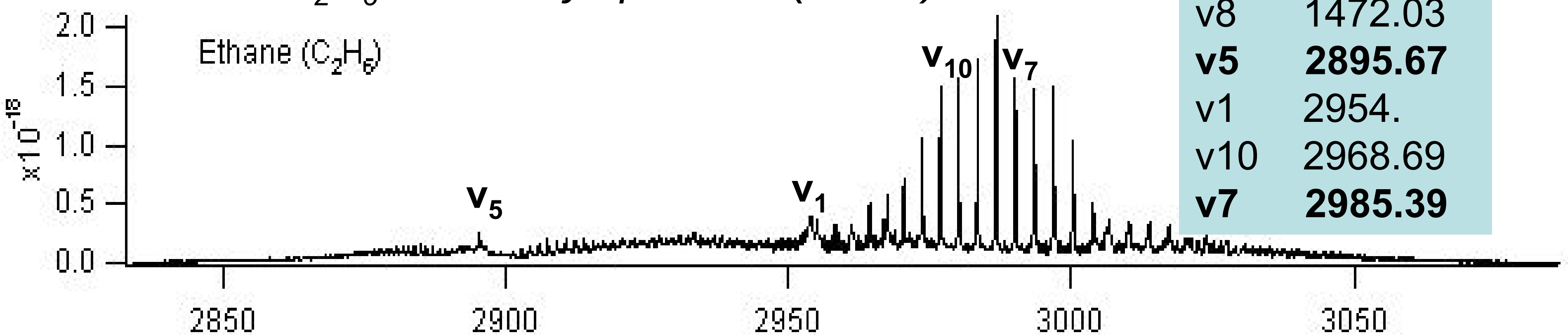
Ethane Spectroscopy 2950-3022 cm^{-1}

Ethane is a strong absorber in the troposphere. The v_7 band centered at 2985 cm^{-1} is by far the strongest. C_2H_6 absorption depths can exceed 50% along limb paths in the tropical troposphere.

Ethane has a complicated spectrum (many interacting vibrational modes), which makes it difficult to accurately predict the spectrum. The 2900 cm^{-1} region is particularly messy with 4 interacting fundamentals, 2 IR-active and 2 inactive.

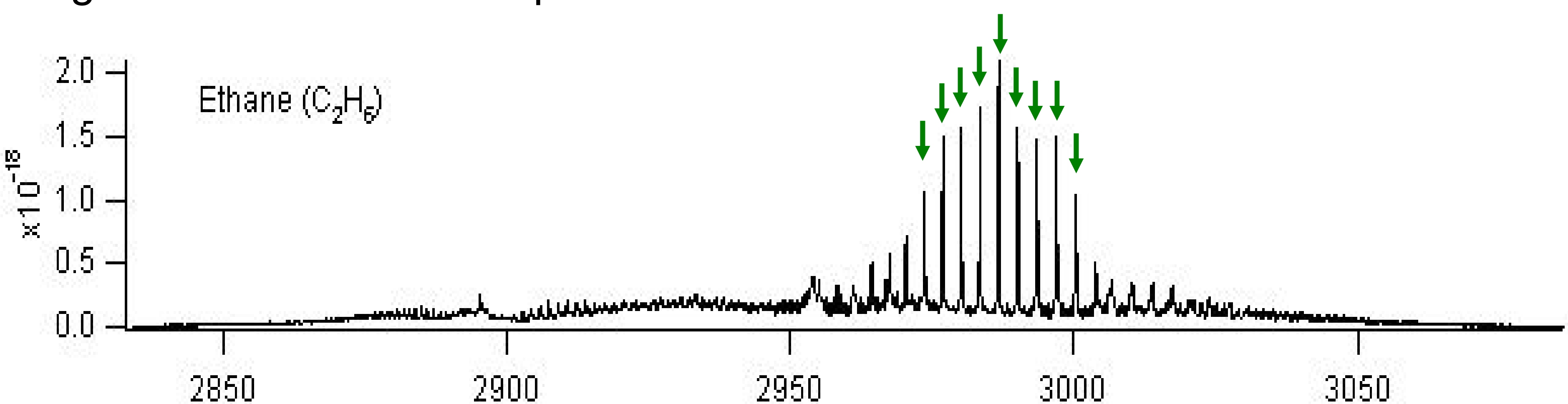
Mode	Freq
v4	289.32
v9	**822.72**
v3	995.11
v12	1195.3
v6	**1379.16**
v2	1397.
v11	1468.1
v8	1472.03
v5	**2895.67**
v1	2954.
v10	2968.69
v7	**2985.39**

A C_2H_6 laboratory spectrum (PNNL).



Spectroscopy History

• Pine & Lafferty (1982, 1984) assigned C_2H_6 transitions from spectra acquired at 156K, but didn't include PQ-branches
• In 1985, in support of ATMOS, Linda Brown developed an empirical linelist for the 9 strongest PQ-branches of C_2H_6 in the 2973-3001 cm^{-1} region (indicated below by green arrows) based on one Kitt Peak spectrum . This was included in the HITRAN_2000 linelist, but not HITRAN_2004
• Pine and Rinsland [1999] developed a quantum-mechanically-based linelist for the PQ_3 branch at 2976 cm^{-1}. This was included in HITRAN_2004.
• PNNL measured C_2H_6 cross-sections from 700-6500 cm^{-1} at 0.1 cm^{-1} resoln
• July 2007 HITRAN C_2H_6 update contains the Pine & Rinsland PQ_3 branch, together with Brown's empirical linelist for the other PQ-branches.



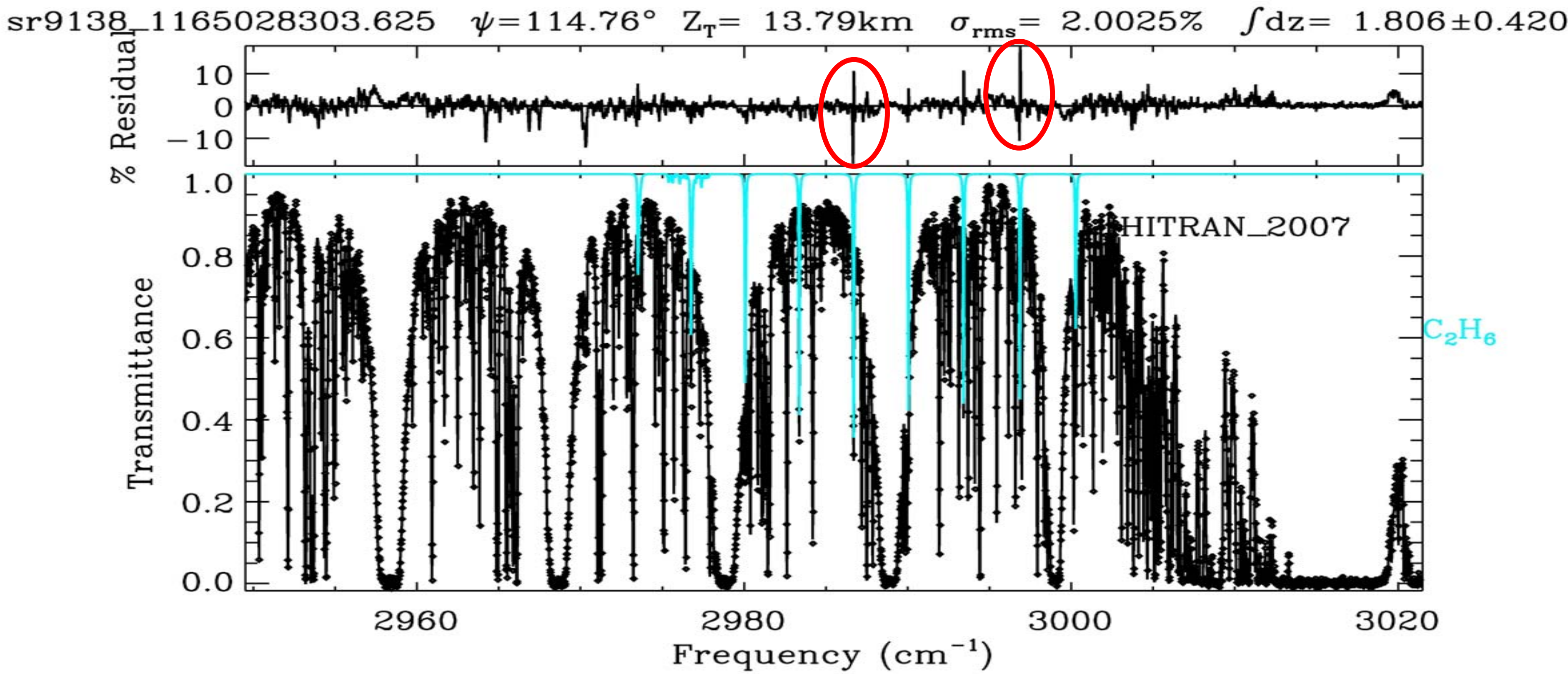
Overview

This presentation will show that the July 2007 HITRAN C_2H_6 update linelist, although much improved in the 820 cm^{-1} region, is inadequate in the 2950-3020 cm^{-1} region where many gases have absorption bands:

1) The missing PQ-branches (below 2973 cm^{-1} and above 3001 cm^{-1}) can have absorption depths exceeding 10% in limb spectra
2) Two of the nine PQ-branches in HITRAN appear frequency-shifted with respect to the other 7
3) The line strengths appear to be 10% too large, referenced to PNNL spectra

Fits to ACE Occultation Spectra

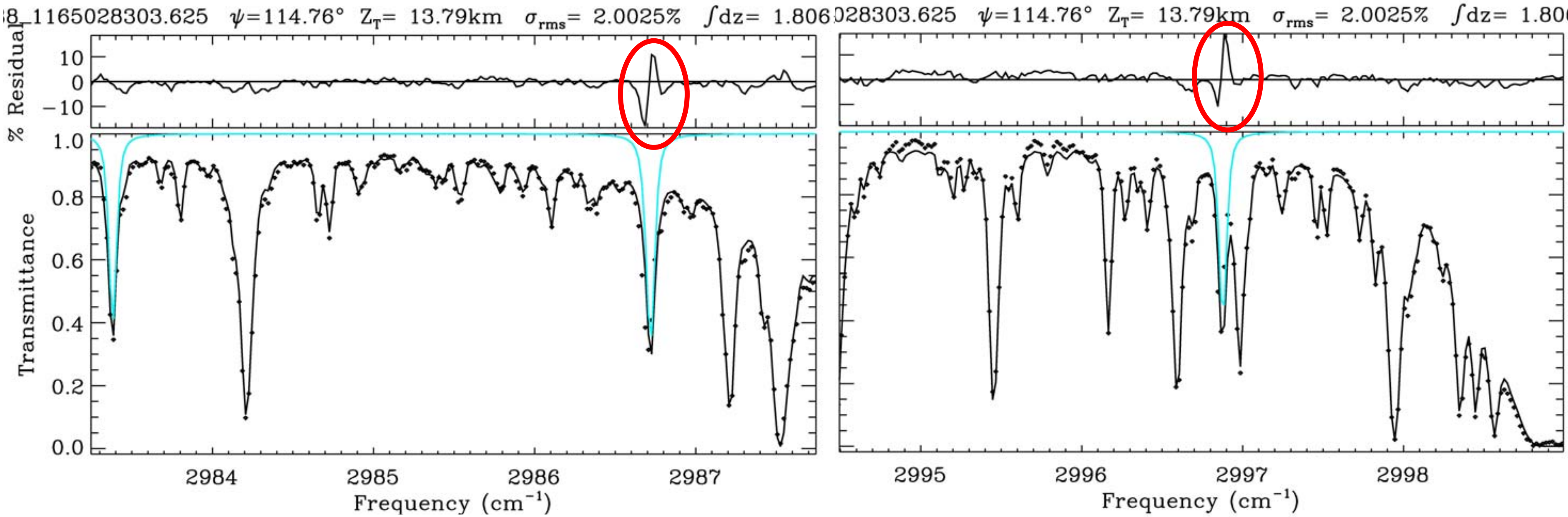
The figure below shows a fit to an ACE spectrum acquired at 13.79 km tangent altitude in the tropics. The main absorbers are CH_4, O_3, H_2O, HCl. The transmittance spectrum of C_2H_6 alone is denoted by the blue line.



The largest residuals appear at the 2986 and 2997 cm^{-1} C_2H_6 PQ-branches

Investigate the two largest residuals

The plots below zoom in on the two largest residuals of the previous figure.



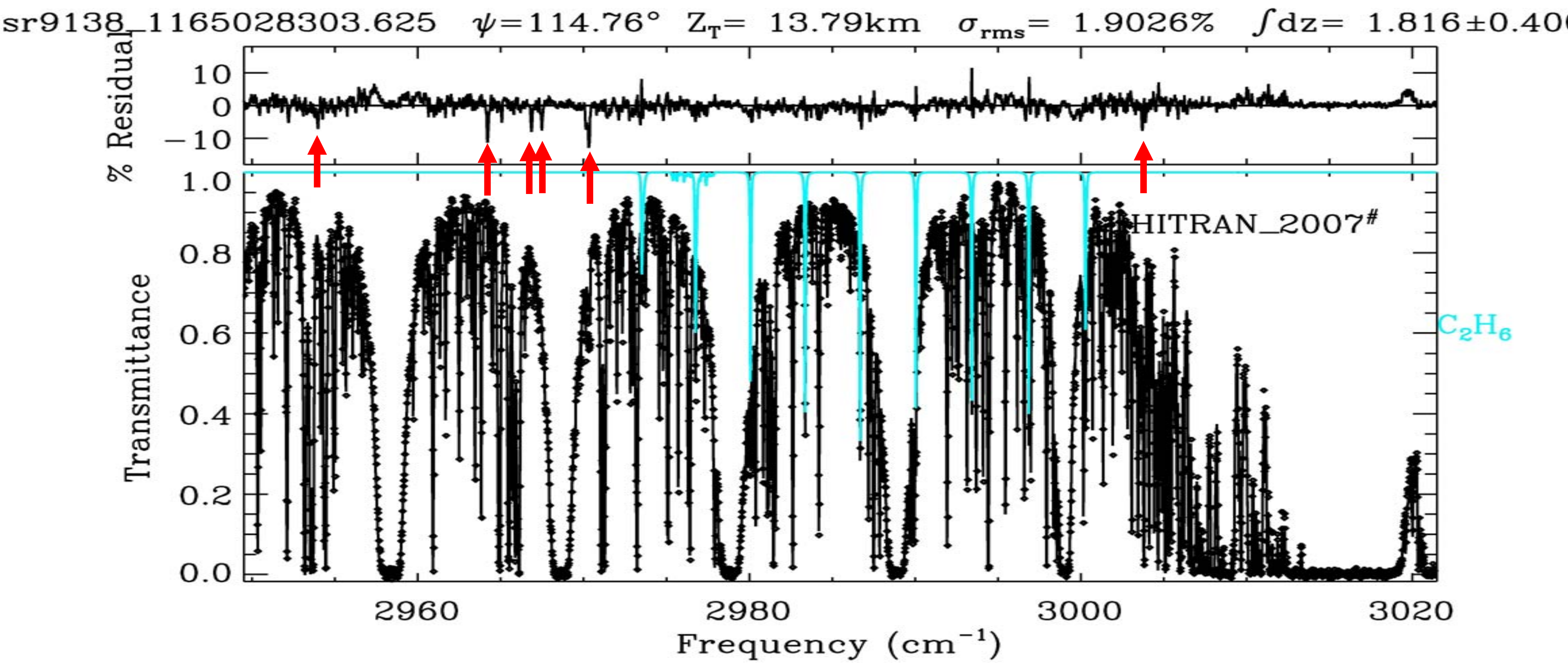
These shifts were corrected by editing the HITRAN 2007 C_2H_6 linelist update:

- subtracted 0.015 cm^{-1} from the line positions of the 2986.7 cm^{-1} PQ branch
- subtracted 0.010 cm^{-1} from the line positions of the 2996.9 cm^{-1} PQ-branch.

I then refitted the entire spectral region using this modified HITRAN_2007 linelist, which is denoted by HITRAN_2007# in the subsequent plots.

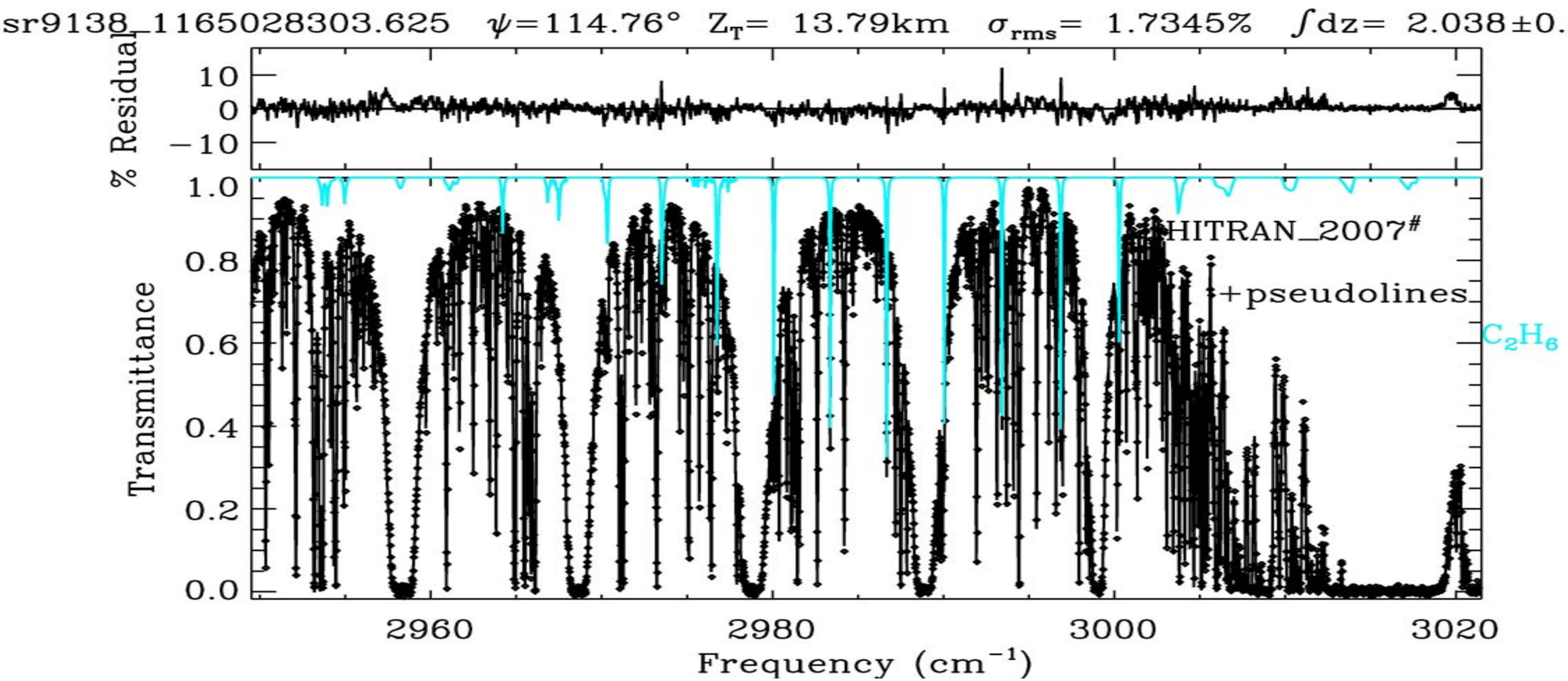
Spectral fit obtained with the frequency-corrected HITRAN_2007# linelist.

The main residuals now correspond to missing PQ-branches of C_2H_6 (red arrows), which exceed 10% in depth in this particular spectrum.



In 1995 I developed a supplemental C_2H_6 pseudo-linelist to represent the absorptions from these missing PQ-branches. This was not intended to improve the retrievals of C_2H_6, but to better fit other gases (e.g. CH_3Cl).

The figure shows the improved spectral fits obtained using the frequency-corrected HITRAN_2007 C_2H_6 linelist plus the supplemental pseudo-linelist.



Despite improvements, the residuals in this interval are still dominated by C_2H_6

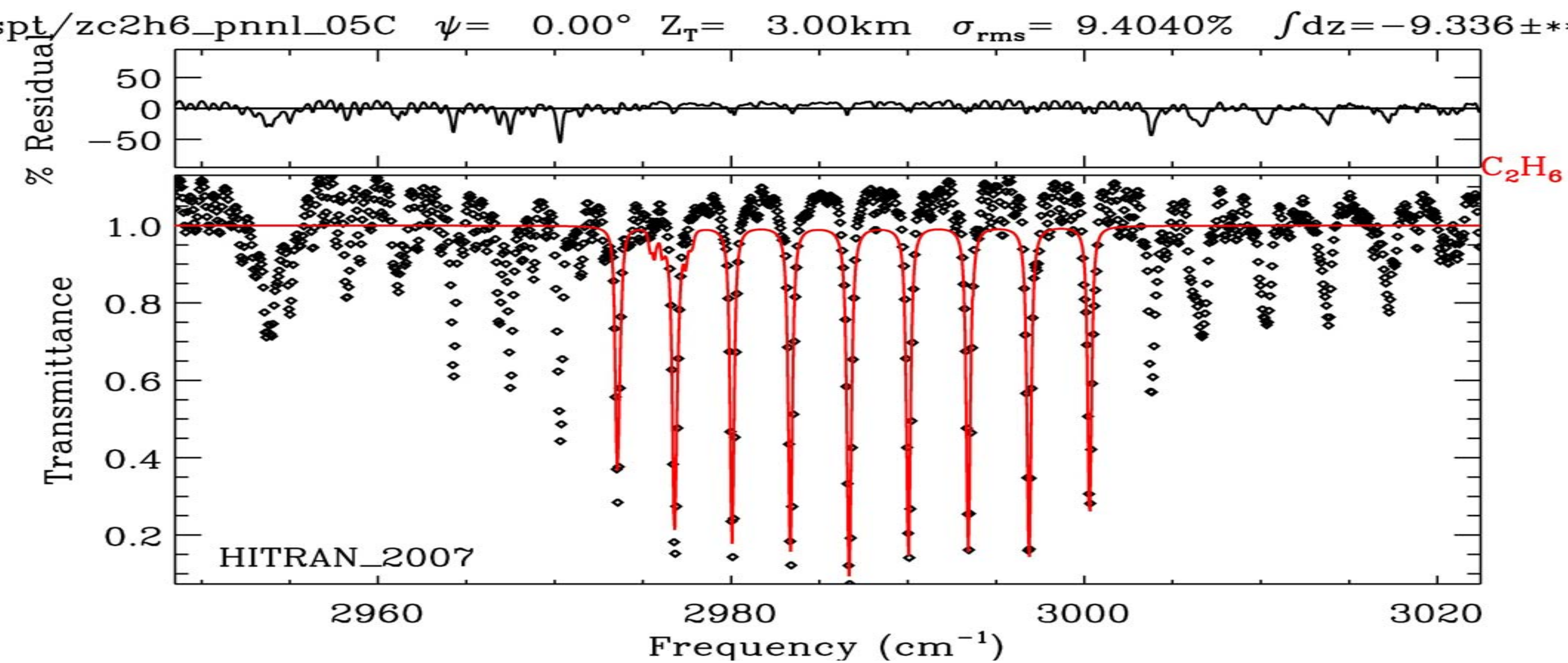
Spectral fits to PNNL Spectra

How do I know that the missing absorptions in the ACE occultation spectra are due to C_2H_6 and not some other gas?

I fitted 0.1 cm^{-1} resolution PNNL (Pacific NorthWest National Laboratory) spectra of pure C_2H_6 using the same linelists used to fit the ACE spectra.

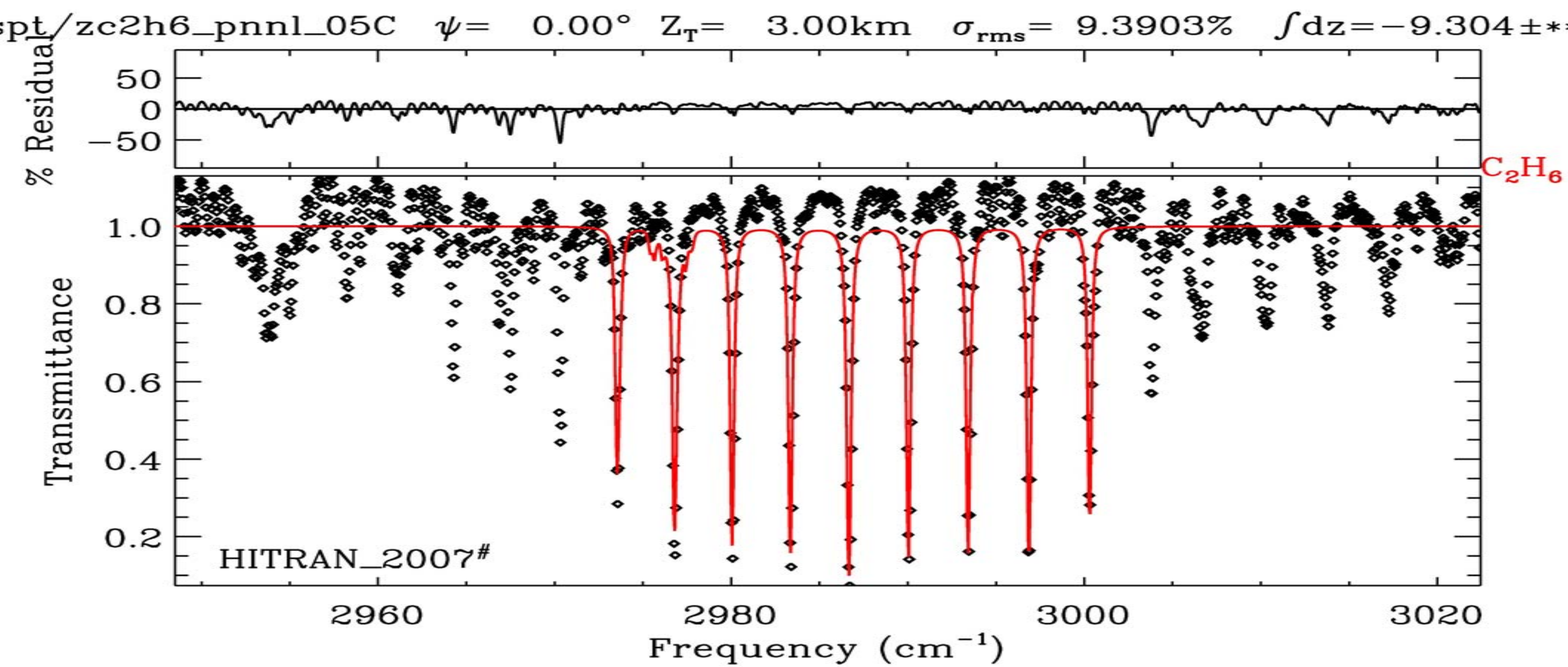
HITRAN_2007

The missing P-Q branches of C_2H_6 are very obvious in this figure showing a fit to a PNNL spectrum measured at 5C and 1 atmosphere.



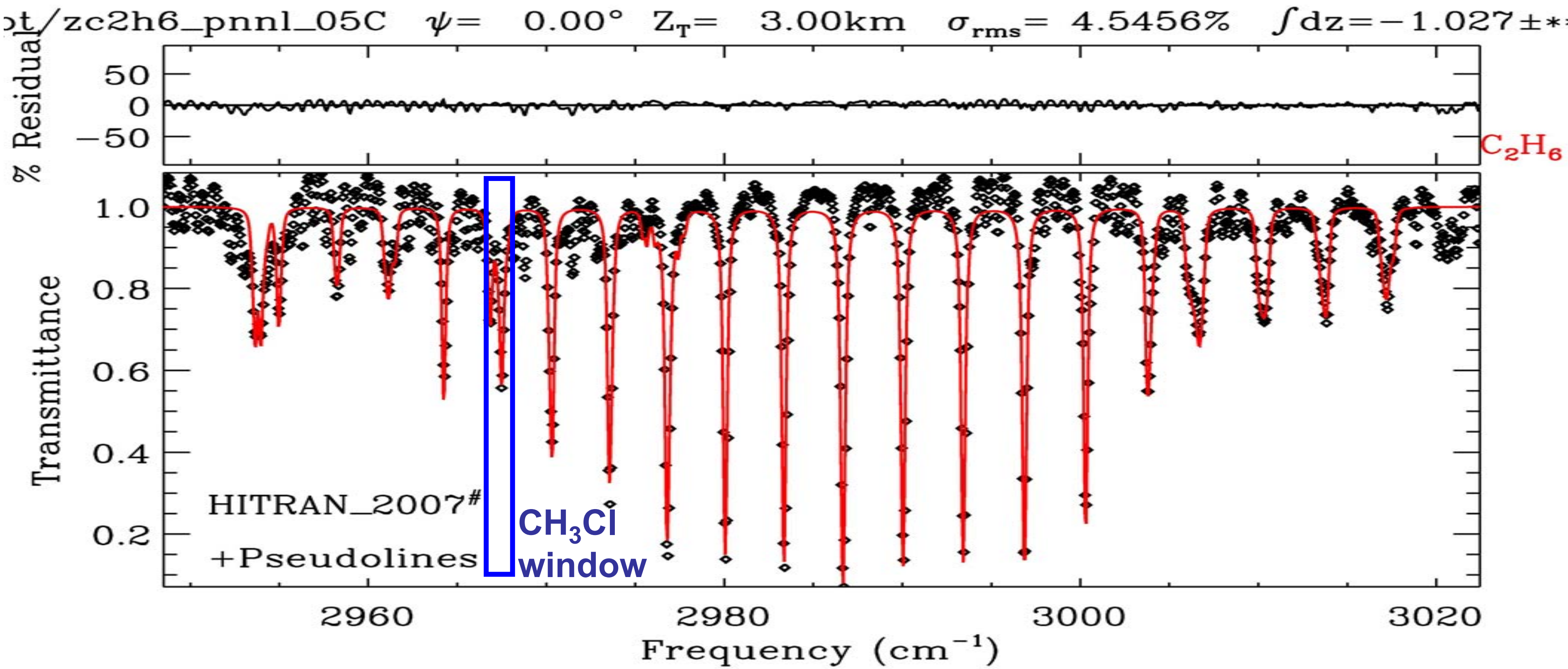
HITRAN_2007#

The frequency-shift-corrected HITRAN_2007 linelist doesn't make a big improvement because the PNNL spectra were acquired at 1 atmosphere

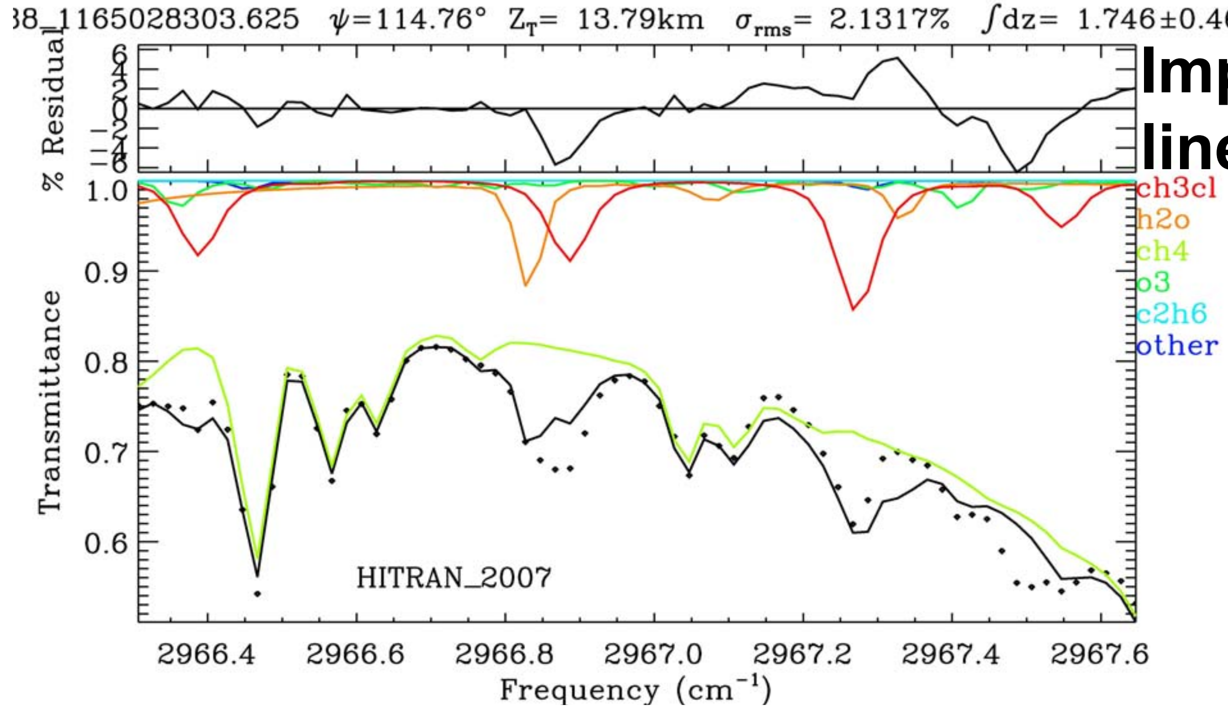


HITRAN_2007# + Pseudo-lines

Including the C_2H_6 supplemental pseudo-lines make a big improvement.

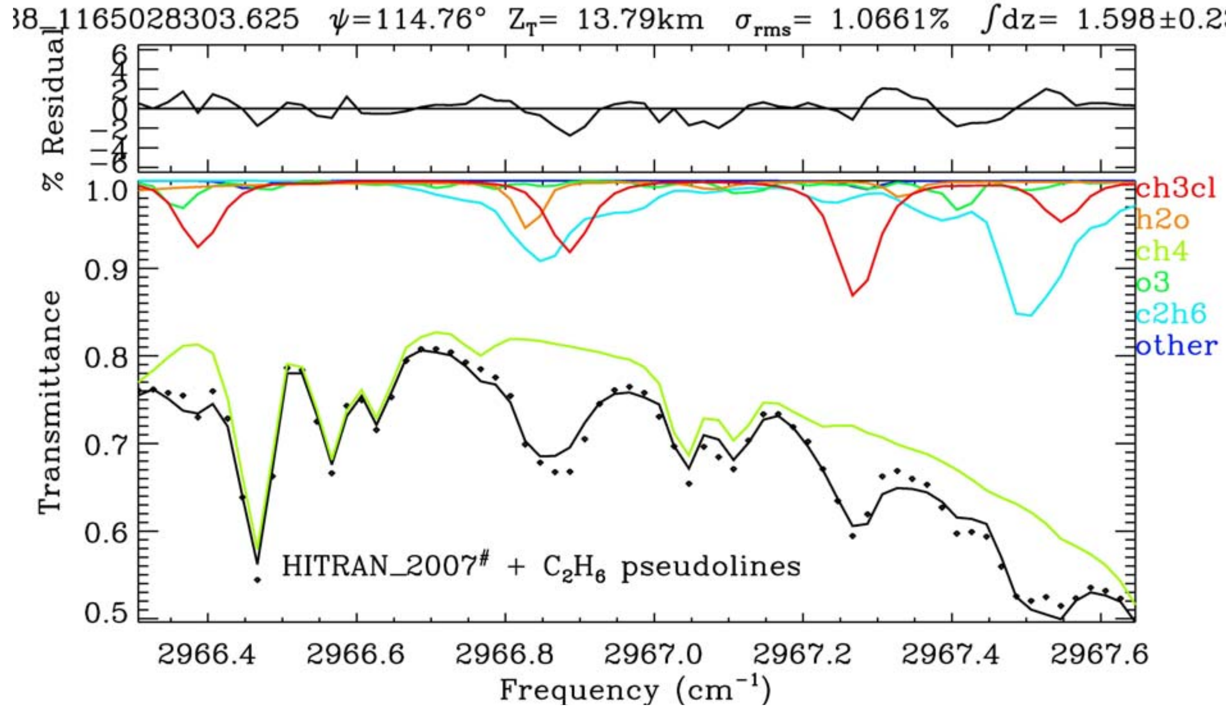


Impact of C_2H_6 pseudo-lines on ACE spectral fits



No C_2H_6 absorption lines in this interval.

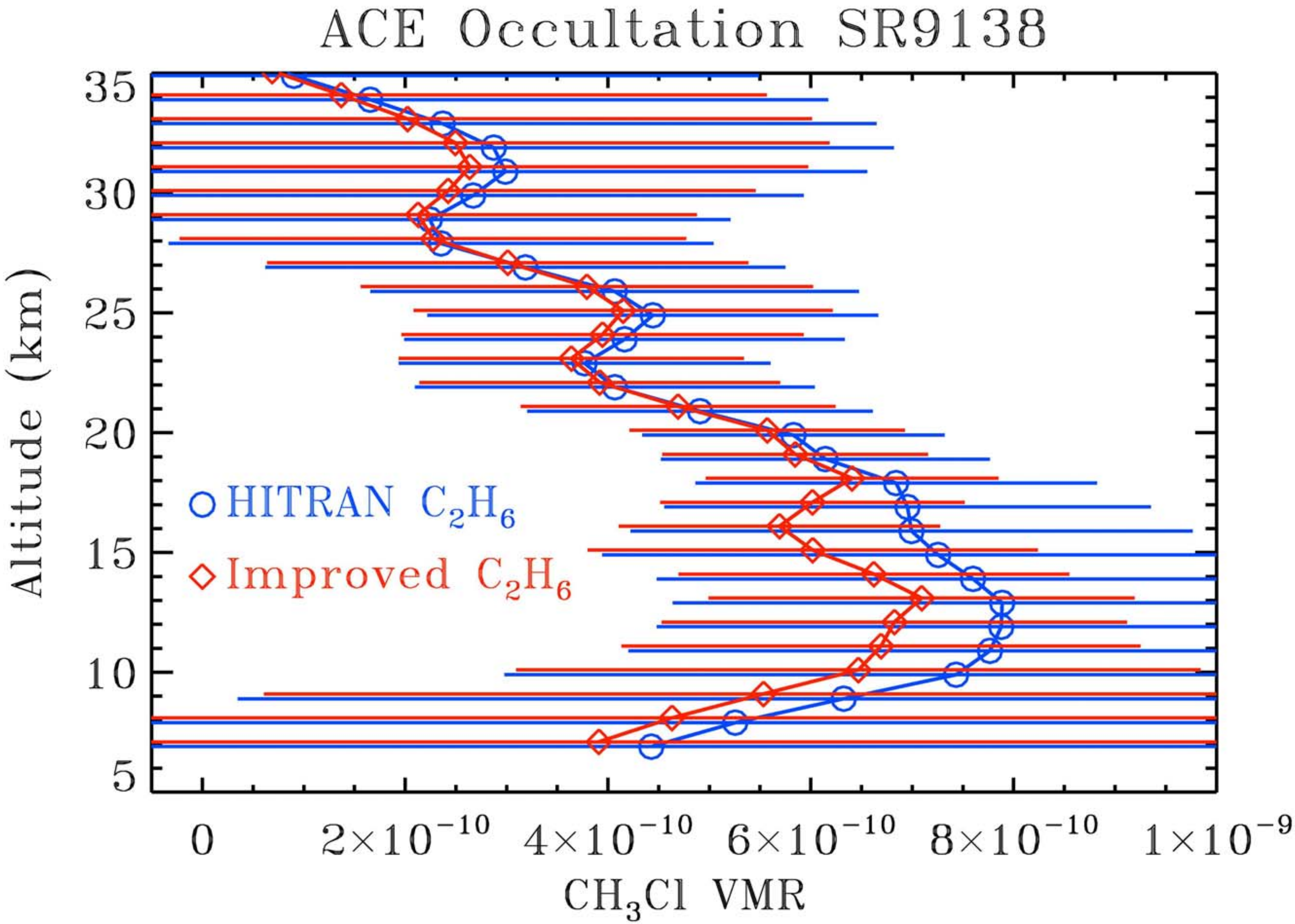
Large systematic residuals due to missing C_2H_6 lines



With supplemental C_2H_6 pseudo-lines.

RMS residual is reduced by a factor 2

Impact on Retrieved CH_3Cl profiles



Summary

The 2950-3020 cm^{-1} spectral region contains absorptions from many gases of interest (e.g. everything having a C-H stretch).

This interval contains the strongest infrared absorptions of C_2H_6, which can exceed 50% in depth in limb spectra of the tropical troposphere.

Although the July 2007 HITRAN C_2H_6 update captures the 9 strongest C_2H_6 PQ-branches, it omits several of the weaker absorptions features which can exceed 10% in absorption depth.

Frequency-corrected HITRAN_2007 linelist, together with supplemental pseudo-lines, do a much better job at fitting tropospheric spectra, but C_2H_6 is still the main cause of residuals.

These residuals can substantially affect retrievals of other minor gases (e.g. CH_3Cl).

Conclusions

We still need a much better C_2H_6 linelist for the 2950-3020 cm^{-1} region.

There exist plenty of high resolution laboratory C_2H_6 spectra acquired at upper tropospheric temperatures (200K) and pressures (200 mbar), e.g. Kitt Peak.

Their quantum-mechanical analysis is very difficult and therefore lacking, with the exception of the PQ_3 branch.

So far, only empirical approaches (e.g. pseudo-lines) have been used for the remaining PQ-branches.